phine complexes are not twice as great as variations in k_2 is still unresolved.

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Notes

Contribution from Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California 91304

Equilibrium Studies of Chlorine Pentafluoride

By H. F. Bauer and D. F. Sheehan

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In the course of our synthesis of chlorine pentafluoride, a new, recently reported interhalogen,[1-3] from chlorine and fluorine, it was found that complete conversion of chlorine to chlorine pentafluoride did not occur, even over extended periods of time and with a tenfold excess of fluorine. The presence of chlorine trifluoride suggested either a very slow reaction or, more probably, that the system was governed by the equilibrium $ClF_3 + F_2 \rightleftarrows ClF_5$, similar to the system $ClF + F_2 \rightleftarrows ClF_3$.[4] A study was undertaken to demonstrate the existence of this equilibrium and to obtain enthalpy and entropy changes for the reaction $ClF_3 + F_2 = ClF_5$.

Experimental Section

Materials.—Fluorine obtained from the Allied Chemical Corporation, chlorine and chlorine trifluoride from the Matheson Company, and chlorine pentafluoride from the Rocketdyne Division of North American Aviation were used in this study. Monel reactors fitted with Monel valves and Ashcroft Monel tube Duragauges were found compatible with the halogens and interhalogens used. Thus, a near equality in the material balance of reactants and products could be assumed. Reactors made from 304 stainless steel proved unsatisfactory in this regard and even the Monel metal was significantly corroded by the fluorine–interhalogen mixtures above 300°, over prolonged periods of time.

Sampling.—A 16-hr period was taken as sufficient to establish equilibrium, temperature control being maintained with the aid of a Wood's metal bath. To sample the equilibrium composition, an isolated small sample was quenched by rapid expansion. Nonuniform composition due to partial condensation in incompletely immersed portions of the apparatus was avoided by maintaining the partial pressure of ClF_3 and ClF_5 below their ambient temperature equilibrium vapor pressures.

Analyses.—The fluorine content of an equilibrium sample was calculated from the difference between the total and condensable gas pressures in a known volume as well as by gas chromatographic separation. The partial pressure of fluorine was calculated from the per cent fluorine and the total equilibrium pressure prior to quenching. Separation was effected with a 20 ft, 0.25 in. column packed with a 50/50 weight ratio of 12-21 halocarbon oil on 30–50 mesh, low-density, Kel-F molding powder.[5] This column was not capable of separating ClF_3 and ClF_5. The chlorine fluorides were separated by vacuum sublimation using −196 and −112° baths. From infrared spectra of the pure components, run under identical conditions, it was possible to estimate the concentration of each fluoride originally present in the equilibrium mixture, with an accuracy within 20%. The spectra were obtained using Monel gas cells fitted with silver chloride windows.

Results and Discussion

The temperature range and equilibration times appropriate for this study were defined by a series of pressure–temperature–time curves for both chlorine trifluoride–fluorine mixtures and chlorine pentafluoride alone. Negative deviations from a Boyle's law behavior, first discernible near 180° for chlorine trifluoride–fluorine mixtures, indicated reaction. Positive deviations during the heating of chlorine pentafluoride were first seen near 200°. Even at 210°, 4 hr was required to ensure that no further pressure changes were taking place. At 217° the rate of dissociation was conveniently rapid; a pressure increase of one-third was observed after 40 min. In the temperature range 211–271° no undesirable side reactions were detected after 16-hr heating periods. Since the rate of formation or dissociation of ClF_5 below 200° was too slow, catalysis of these reactions was investigated. Attempts to catalyze equilibration at lower temperatures with AgF_2, BF_3, or increased surface were unsuccessful.

The equilibrium constant, $K_p = P_{ClF_5}/P_{ClF_3}P_{F_2}$, was calculated from the ratio of the partial pressures of ClF_5 and ClF_3 and from the partial pressure of fluorine under equilibrium conditions. The results of eight determinations at various temperatures are shown in Table I. Determination of the ratio P_{ClF_5}/P_{ClF_3} by infrared analysis[6,7] was affected by certain errors inherent in this technique. The method of determining absorbances was by difference from background on a logarithmic scale. Errors in the estimate of the relative concentrations of ClF_3 and ClF_5 undoubtedly accrued from the variation in cell background and pen response, but it is possible that additional inaccuracy arose from some interaction of the fluorine and fluorides with the less inert parts of the containers, *e.g.*, the

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TABLE I

EQUILIBRIUM CONSTANT DATA AT 211–271°

($K_p = P_{ClF_5}/P_{ClF_3}P_{F_2}$)

T, °K	$10^2(P_{ClF_5}/P_{ClF_3})$	P_{F_2}, atm	10^2K_p, atm^{-1}
484	27.9	3.27	8.52
486	26.8	3.43	7.80
493	25.5	3.44	7.40
497	24.8	3.52	7.06
516	11.1	3.58	3.10
518	9.28	3.60	2.58
542	5.01	3.71	1.35
544	3.99	3.84	1.04

AgCl windows and the halocarbon wax. Most of the errors were systematic and probably affected ClF_3 and ClF_5 values similarly. Since K_p is proportional to the ratio P_{ClF_5}/P_{ClF_3}, systematic inaccuracies in the infrared analysis tend to cancel. Moreover, thermodynamic functions derived from these data involved the logarithm of this ratio and thus are insensitive to errors in the infrared analysis. The data were fitted to the van't Hoff equation, $\ln K_p = 9175/T - 21.30$, by the method of least squares and are plotted in Figure 1. By expressing the equation in the form $\ln K_p = -(\Delta H_r/RT) + (\Delta S_r/R)$, the enthalpy and entropy of reaction in the temperature range near 240° were obtained: $\Delta H_r = -18.2 \pm 0.9$ kcal and $\Delta S_r = -42.3 \pm 1.8$ eu. Although the data were fitted to an equation with a standard deviation of 5%, the straight-line fit should not be interpreted as a measure of the accuracy of the data. Using $\Delta H_{f\,500}(ClF_3(g)) = -37.8$ kcal/mole from the JANAF tables, the authors calculate $\Delta H_{f\,500}(ClF_5(g)) = -56.0$ kcal/mole.

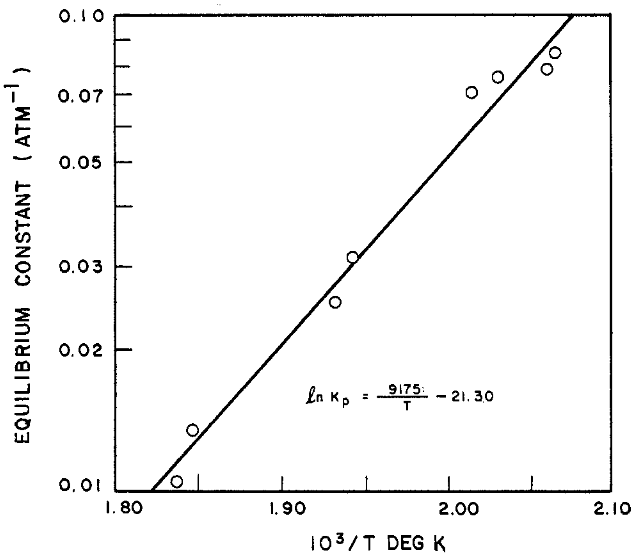

Figure 1.—Equilibrium constant as a function of temperature ($K_p = P_{ClF_5}/P_{ClF_3}P_{F_2}$).

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An Interpretation of the Proton Hyperfine Splitting in the Electron Paramagnetic Resonance Spectrum of Vanadyl-Doped Zinc Tutton Salt[1]

BY W. BURTON LEWIS

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Ordinarily the proton hyperfine splitting in hydrated ions of the iron group transition metals is too small to be resolved in epr spectra and contributes only to line broadening. Borcherts and Kikuchi,[2] however, report the resolution of a five-line superhyperfine structure superimposed on the normal eight V^{51} hyperfine components of the $VO(H_2O)_5^{2+}$ epr spectrum present as a 0.5% impurity in single crystals of the Tutton salt $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$. They confirmed that protons are the source of the splitting by examining crystals grown from D_2O solution. A crystal grown from ordinary water gave a 5-gauss superhyperfine splitting only when the static magnetic field H was directed parallel to one of the four V–O bonds to water molecules in a plane perpendicular to the shortest V–O bond (1.67 A). With the field along other directions, the superhyperfine structure disappeared. In particular, the maximum slope line width of a V^{51} hyperfine component for H parallel to the short V–O bond was 8–10 gauss, and for H bisecting the angle between two V–O bonds to adjacent water molecules in the plane perpendicular to the short V–O bond the line width was about 20 gauss. The line widths for a crystal grown from D_2O on the other hand were reduced by a factor of three.

The explanation of a five-line proton hyperfine structure with relative intensities in the ratio 1:4:6:4:1 and a splitting of 5 gauss is not immediately obvious. The coordination number of the VO^{2+} ion is normally five or six including the oxygen ion, and one expects therefore a minimum of four water molecules to be coordinated to this ion. Using the structural analysis of Montgomery and Lingafelter[3] for $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$, it can be shown that the dipolar fields arising from the various spin configurations possible with the eight nearest protons yield a spectrum with many components but bunched into 13 distinct groups (for H in the direction of the observed splitting). The separation between groups of lines is 2 gauss and the total spread of the spectrum is 17 gauss. Adding a fifth water molecule at the position opposite the vanadyl oxygen ion would only increase the complexity and spread of this spectrum. While it appears that no reliable estimate has been made of the proton iso-

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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